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Tracing subducted black shales in the Lesser Antilles arc using molybdenum isotope ratios

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ABSTRACT

Lesser Antilles arc lavas have trace element and radiogenic isotope characteristics indicative of a continent-derived contribution. It is hotly debated whether this continental signature represents terrigenous sediment that has been subducted with the Atlantic plate and added to the magma sources in the mantle wedge or portions of the sub-arc crust that are assimilated during magma ascent. Here we present Mo isotope data for Lesser Antilles arc lavas and sediments off-board the Lesser Antilles trench. Sequences of black shales, present in the subducting sediment piles, are highly enriched in Mo and have unusually high $^{98}Mo/^{95}Mo$. Despite their low mass fraction in the sediment package (<10 % in DSDP Site 144), they dominate the Mo content and isotopic composition of the bulk sediment subducting at the Lesser Antilles trench. We show that lavas from the southern part of the Lesser Antilles arc also have high $^{98}Mo/^{95}Mo$ ratios, implicating the addition

of Mo derived from the subducted black shales to their mantle sources. This establishes a new link between the composition of subducted material and the arc lava output.

INTRODUCTION

Molybdenum isotope ratios provide an important means of tracing paleo-redox conditions in the ocean. Among the many different oceanic sediment types, black shales are of special interest for Mo isotope studies because they have unusually high Mo concentrations and are associated with heavy Mo isotope ratios that record the composition of contemporaneous seawater when depositional conditions are pervasively euxinic (Barling et al. 2001, Gordon et al., 2009). Hence black shales constitute a high $^{98}Mo/^{95}Mo$ end-member among oceanic sediments. Under more oxidizing conditions lighter Mo isotopes are preferentially incorporated into sediments (Barling et al. 2001).

The unique signature of high Mo concentrations and high $^{98}Mo/^{95}Mo$ ratios provides an attractive means to trace the fate of black shales after they have been subducted. Sequences of black shales deposited in the Atlantic ocean as a result of Cretaceous oceanic anoxic events (OAEs) are currently being subducted at the Lesser Antilles trench. Black shales from OAE 2 and OAE 3 (84–93 Ma) have been sampled at DSDP Site 144. Carpentier et al. (2008) concluded that a component derived from these black shales is likely transported into the Lesser Antilles arc magma sources based on their highly radiogenic Pb isotope ratios. However, the view that the isotopic compositions of the Lesser Antilles lavas are related to subducted sediments remains contentious (e.g., Thirlwall and Graham, 1984; Davidson, 1986; White and Dupré, 1986; Thirlwall et al., 1996; Turner et al., 1996; Carpentier et al., 2008; Labanieh et al., 2010). Most recently, it has been suggested that crustal assimilation could explain the isotopic variability in lavas from St. Lucia, assuming that the southern Lesser Antilles arc is built upon the older Aves ridge (Bezard et al. 2014). In addition, the highly radiogenic Pb isotope composition of some Lesser Antilles arc lavas could be related to melting sediments similar to those found on the over-riding plate in Barbados rather than subducting black shales (Carpentier et al., 2008). The possibility of combining a novel tracer for components derived from subducted black shales in Lesser Antilles arc magmas with other geochemical fingerprints could therefore offer important new information on the long-standing controversy regarding the importance of subducted sediments in Lesser Antilles magmas.

MOLYBDENUM ISOTOPE COMPOSITION OF SEDIMENTS SUBDUCTING AT THE LESSER ANTILLES ARC

There has been extensive previous work geochemically characterizing the sediments on the Atlantic plate near the Lesser Antilles trench, with the aim of constraining subduction inputs (White et al., 1985; Carpentier et al., 2008; Carpentier et al., 2009), including analyses of samples drilled at DSDP Sites 144 and 543 (Fig. DR1). DSDP Site 543 is located close to the Lesser Antilles arc on oceanic crust of Campanian (ca. 80 Ma) age. DSDP Site 144 is located further from the trench than DSDP Site 543, on the Demerera rise southeast of the Lesser Antilles trench (Fig. DR1). Black shales deposited during OAE 2 and OAE 3 (84–93 Ma) have been sampled at DSDP Site 144 but are not present at the younger DSDP Site 543 where the oceanic crust formed after the deposition of the black shales. For the purposes of this study, we therefore focus on sediments of DSDP Site 144.

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Our measurements of Mo isotope ratios and Mo concentrations in representative sediment samples from the different lithological units of DSDP Site 144 (reported in Table DR1) are shown in Fig. 1, together with sediment samples from ODP Sites 800, 801 and 802. The latter sites are located on ca. 167 Ma Pacific crust near the Mariana trench and are the only other oceanic sediment columns that have been analyzed for Mo isotope ratios (Freymuth et al., 2015). Of all the sediments analysed from the Pacific and Atlantic sites, black shales have the highest $\delta^{98/95}$Mo (the permil variation in ^{98}Mo/^{95}Mo relative to the NIST 3134 standard) and the highest Mo concentrations. The Mo isotope composition of the DSDP Site 144 black shales ($\delta^{98/95}$Mo ~0.6) is within the range of previously reported data for OAE 2 black shales from DSDP Site 367 and drill site S57 in the NE Atlantic ($\delta^{98/95}$Mo approx. 0.45 – 0.85, Westermann et al., 2014; Goldberg et al., 2016).

The calculated Mo isotope ratio of the bulk sediment at DSDP Site 144 (see caption to Fig. 1) is dominated by the black shale contribution and it is ~0.8 permil higher in $\delta^{98/95}$Mo than the bulk ODP Site 801 sediment. It also greatly exceeds the estimated ranges in $\delta^{98/95}$Mo of the upper mantle (Freymuth et al., 2015; Greber et al., 2015), bulk silicate earth (Burkhardt et al., 2014; Greber et al. 2015), and the continental crust (Siebert et al. 2003; Voegelin et al. 2014) (Fig. 1).

TRACING SUBDUCTED BLACK SHALES WITH Mo ISOTOPES

Within the Lesser Antilles arc lavas there is a substantial, though in detail complex, gradient of radiogenic isotope ratios with more ‘continental’ compositions in the southern islands than in the northern islands, e.g., Sr and Pb isotope ratios become more radiogenic and Nd isotope ratios become less radiogenic southwards (White and

Dupré, 1986; Turner et al., 1996; Macdonald et al., 2000; Carpentier et al., 2008) (Fig. DR2). We have analyzed samples from along the arc that are already well-characterized for Sr-O-He isotopic compositions (van Soest et al., 2002). The sample set encompasses much of the isotopic variability along arc from 'depleted' signatures in the north to more continental compositions in the south (Fig DR2).

With the exception of the sample from Martinique, Mo isotope ratios in the Lesser Antilles lavas are unrelated to the degree of differentiation (Fig. 2a) but correlate with radiogenic Sr and Pb isotope ratios and Ce/Mo (Fig. 2b-d). As with the radiogenic isotopes, the Mo isotope and Ce/Mo ratios of the Lesser Antilles arc lavas show a regional variation with higher $\delta^{98/95}$Mo and Ce/Mo in the southern islands than in the northern islands.

We have focused on mafic samples and the most primitive magmas, from southern islands, have the highest $\delta^{98/95}$Mo (Fig. 2a). Thus there is no scope to explain the unusually $\delta^{98/95}$Mo in the southern islands as a result of fractionation of hydrous phases (Voegelin et al., 2014), that are anyway absent as phenocryst phases in most of our samples (Table DR1). Assimilation of crustal basement has been suggested to explain some of the geochemical heterogeneity in the Lesser Antilles, in particular in the Central islands (e.g., Davidson, 1986; Macdonald et al., 2000; Bezard et al., 2014). Again we note that the highest $\delta^{98/95}$Mo ratios are present in samples from the southern islands (Fig. 2a) and include the most primitive lava sample from the Lesser Antilles (van Soest, 2000). This sample has mantle-like Os isotope ratios and was unaffected by crustal assimilation (Bezard et al., 2015a). It is therefore highly unlikely that the elevated Mo isotopic ratios documented here are related to assimilation of sub-arc crust. An exception might be our most differentiated, andesitic sample from Martinique that has the lowest $\delta^{98/95}$Mo (Fig. 2a). A role for crustal assimilation has been documented for lavas from Martinique in order to account for their extreme Sr and Nd isotopic compositions (Figure DR2). The composition of the sub-arc crust is largely unknown but has been suggested to be partly formed by an ancient accretionary prism of the Aves Ridge system (Macdonald et al., 2000). The Carribean plate on which the Aves Ridge is built originates from the Eastern Pacific (Sykes et al., 1982; Burke, 1988) which remained oxic at least during OAE 2 (Takashima et al., 2011), suggesting that the sub-arc crust has a composition more similar to typical oceanic sediments with low $\delta^{98/95}$Mo (Fig. 1) and so could account for the isotopically light Mo isotope composition of our Martinique sample.

Molybdenum is similarly incompatible during mantle melting to Ce (Newsom et al., 1986). Ratios of Ce/Mo in arc lavas below upper mantle values should therefore reflect preferential slab addition of Mo to the arc lava source (Freymuth et al., 2015). Freymuth et al. (2015) showed that the Mo budget of Mariana arc lavas is dominated by the addition of low Ce/Mo fluids with high $\delta^{98/95}$Mo (~0.05) derived from the subducted, mafic oceanic crust and high Ce/Mo melts with similar or lower $\delta^{98/95}$Mo. Arc lavas with a more dominant influence of sediment melts are typically characterized by lower $\delta^{98/95}$Mo (König et al., 2016), with values as low as −0.7 ‰. Radiogenic isotope ratios of the northern Lesser Antilles lavas indicate they are less influenced by ‘continental’, sediment-like material (Fig. 2b, c, Fig, DR2) and so should have a more 'fluid-dominated’ signature. By analogy with the Mariana arc lavas and supported by the high fluid-mobility of Mo compared to the rare earth elements (Green and Adam, 2003; Bali et al., 2012) we therefore interpret their low Ce/Mo ratios to reflect the addition of Mo-rich fluids to their mantle sources. The Mo isotopic composition of the northern Lesser Antilles lavas suggests a fluid composition of $\delta^{98/95}$Mo ~ −0.15 (Fig. 2d) which slightly lower than that inferred for the Mariana arc (Freymuth et al., 2015).

The high Ce/Mo and radiogenic Sr and Pb isotope composition in the southern Lesser Antilles (Fig. 2) clearly require another component with high $\delta^{98/95}$Mo in addition to slab-derived fluids. The altered top part of the mafic oceanic crust (AOC) has a moderately heavy Mo isotope composition yet a major contribution by the AOC is inconsistent with its unradiogenic Pb isotope composition (Fig. 2c). Among all sediment types, only the black shales have suitably high $\delta^{98/95}$Mo to constitute this component, suggesting that the high $\delta^{98/95}$Mo is derived from the black shales.

Figure 2d shows that the high $\delta^{98/95}$Mo end-member required for the Lesser Antilles arc lavas is also characterized by high Ce/Mo ratios (>35), which is initially a surprise given the low Ce/Mo of the black shales and bulk DSDP Site 144 sediment. Yet, Ce concentrations in hydrous melts derived from certain sediment types can be increased relative to starting compositions if the residual assemblage lacks a host that is as efficient in retaining Ce (e.g., Skora and Blundy, 2010; Martindale et al., 2013). Although the Ce/Mo of the subducted bulk sediment is low, associated experimental work on the Lesser Antilles sediment documents that its melts will likely have higher Ce/Mo (Skora et al, in review).

Carpentier et al. (2008), White and Dupré (1986) and Bezard et al. (2015b) argued for a changing sediment composition toward the northern Lesser Antilles to explain some of the compositional variation in the Lesser Antilles arc magmas. In particular, Carpentier et al. (2008) argued that the black shale sequence is absent beneath the northern Lesser

Antilles arc because the crust in the northern part appeared to be younger than the age of the black shales. Such a scenario is principally consistent with our new data set given that a black shale component is not prominent in that section of the arc. A closer examination of the seafloor magnetic anomalies in the area (Fig. DR1), however, shows that the oceanic crust underneath some of the northern islands is likely >93 Ma old and could thus carry the entire sequence of OAE 2 and OAE 3 black shales sampled at DSDP Site 144.

The lower $\delta^{98/95}$Mo and Ce/Mo in combination with less radiogenic Sr and Pb isotope ratios in the northern Lesser Antilles islands therefore argue for the model of Turner et al. (1996) who proposed a lower contribution of sediment melts to the sources of the northern islands. This could be achieved, for example, if the slab-top temperature beneath the northern Lesser Antilles were lower than beneath the southern arc section, thus inhibiting melting of the slab beneath the northern Lesser Antilles. This scenario is supported by current models of the subduction zone thermal structure that indeed suggest slab top temperatures are lower by approx. 50°C in the northern part of the arc (Syracuse et al., 2010). Alternatively, melting of the sediment section of the slab beneath the northern Lesser Antilles could be inhibited by a low supply of H_2O, as suggested to explain variable degrees of slab melting beneath the Izu arc (Freymuth et al., 2016). Regardless of the underlying process, the along-arc compositional variation in the Lesser Antilles lavas likely reflects changes in the physical parameters of the subduction zone rather than variable input compositions.

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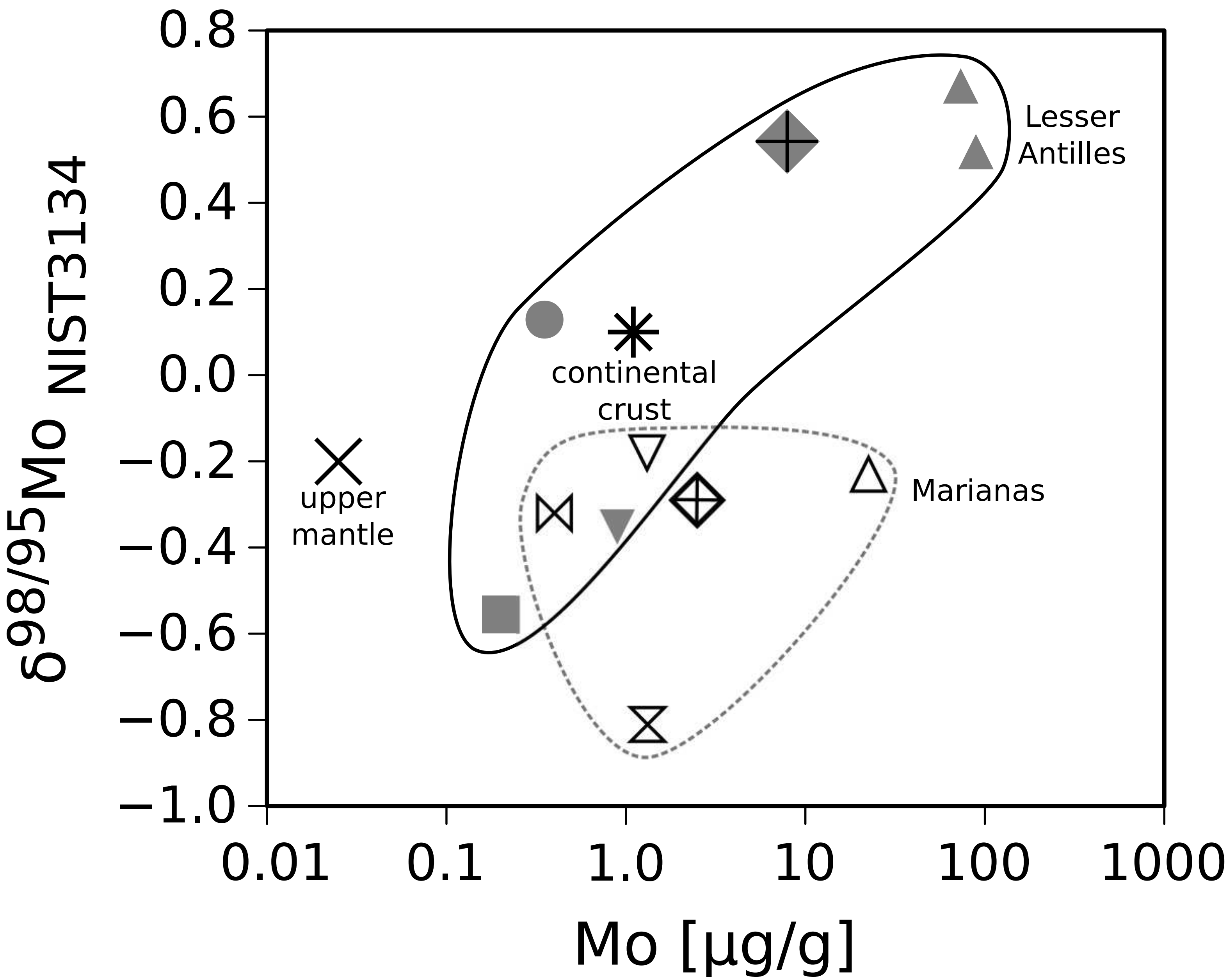
FIGURE CAPTIONS

Figure 1. Mo concentrations and Mo isotope ratios in oceanic sediments from DSPD Site 144 (table DR1) and ODP Sites 800, 801, and 802 (Freymuth et al., 2015). Sediment units and their stratigraphic thickness in DSPD Site 144 are from Hayes et al. (1972). A

representative sample from each of the five units was analyzed, except for unit 4 of which only 1.5 m from a total thickness of 40 m were recovered. ‘Continental crust’ and ‘Upper mantle’, indicate estimates for $\delta^{98/95}$Mo of the bulk continental crust (Voegelin et al., 2014) and upper mantle (Freymuth et al., 2015; Greber et al., 2015) with Mo concentration from Wedepohl (1995) and Salters and Stracke (2004), respectively.

Figure 2. Mo isotope systematics in Lesser Antilles arc lavas. a) $\delta^{98/95}$Mo versus MgO. b) $\delta^{98/95}$Mo versus $^{87}Sr/^{86}Sr$. c) $\delta^{98/95}$Mo versus $^{208}Pb/^{204}Pb$. d) $\delta^{98/95}$Mo versus Ce/Mo. The error bars indicate the 2σ standard deviation of replicate analyses of JB-2 (see DR for details). Dotted line in d) is a linear regression through the Lesser Antilles arc lavas (R^2 = 0.51, excluding sample LSM2 from Martinique, see text for details). The gray area in d) indicates the suggested composition of a slab-derived fluid. Data for the Lesser Antilles arc lavas and sediments are from Table DR1. Upper mantle Mo isotope ratios are from Freymuth et al. (2015) and Greber et al. (2015); Sr and Pb isotope ratios are the average and standard deviation for MORB (compilation of Elliott et al., 1999), and Ce/Mo ratios are the average and standard deviation from Gale et al. (2013). ‘AOC’ is the super composite sample of altered oceanic crust from ODP Site 801 (Kelley et al., 2003, Mo isotope ratios and Mo concentrations from Freymuth et al., 2015). Samples from other arcs in d) are basalts, basaltic andesites, and boninites from the Mariana arc, Solomon arc, Bismarck arc, and Cyprus (Freymuth et al., 2015, König et al., 2016).

[1]GSA Data Repository item 2016xxx, xxxxxxxx, is available online at



Lesser Antilles Sediments
(DSDP Site 144)

- ▼ chalk ooze, unit 1 (120 m)
- ■ mudstone, unit 2 (60 m)
- ▲ black shales, unit 3 (60 m)
- ● carbonaceous clay, unit 5 (47 m)
- average

Marianas sediments
(ODP Leg 129)

- △ Cenozoic clay
- ▽ chert & porcellanite
- ⋈ volcaniclastics
- ⧗ Mesozoic radiolarite & claystone
- average

Figure 2

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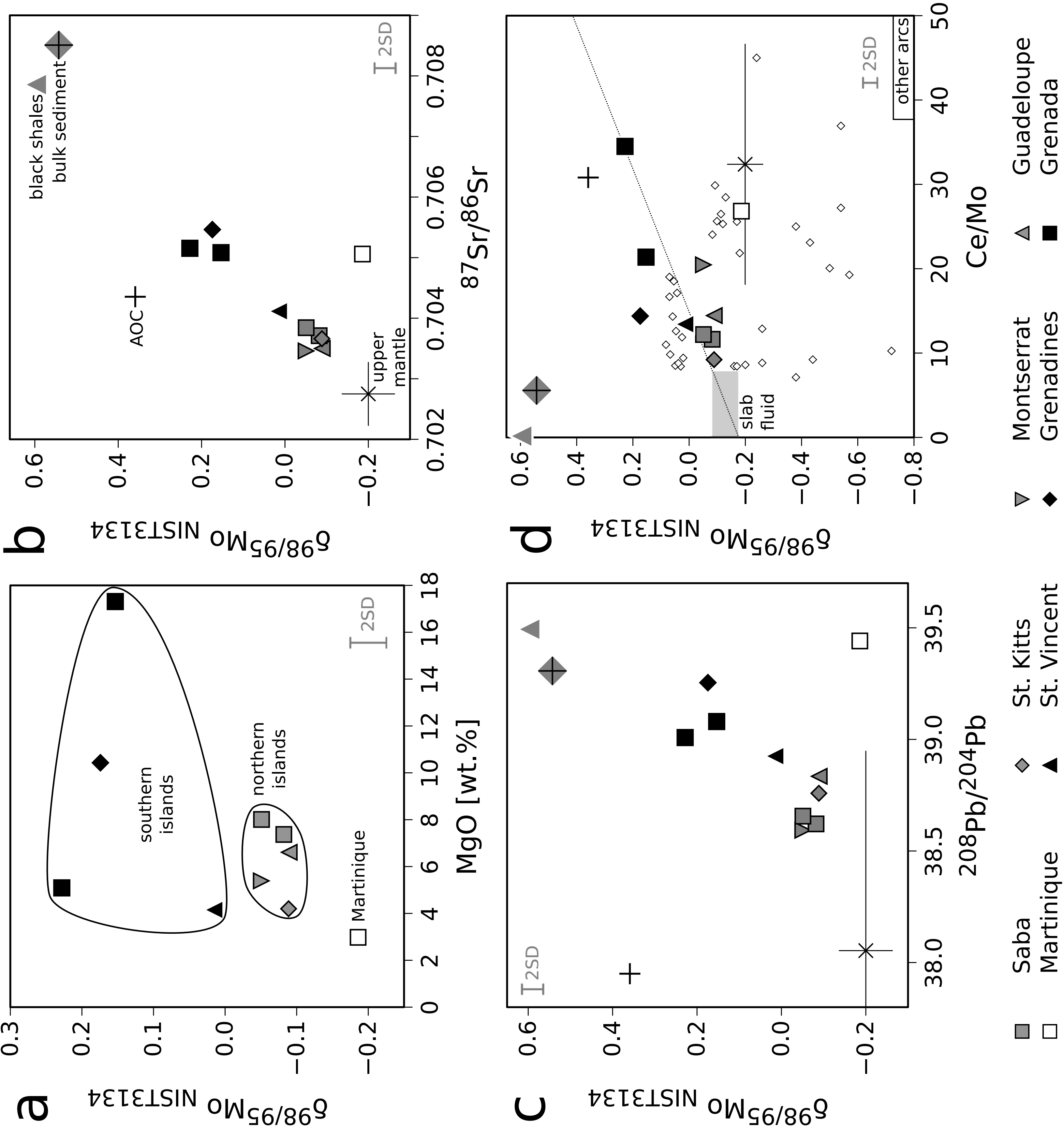

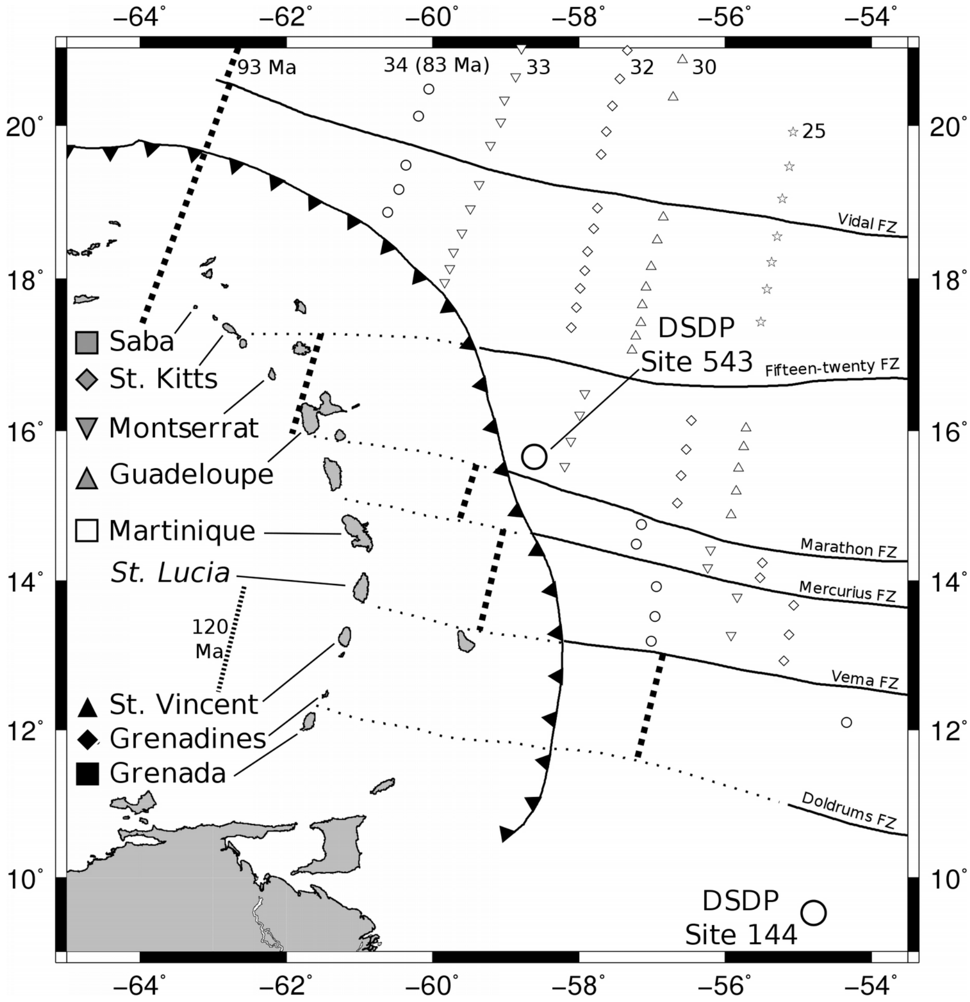

Figure DM1. Map of the Lesser Antilles arc. Oceanic fracture zones (FZ) and projections of the fracture zones into the subduction zone (from Schlaphorst et al., 2016) are shown by solid black lines and dotted black lines, respectively. Seafloor magnetic anomalies are plotted in circles (anomaly C34o, 83 Ma), inverted triangles (anomaly C33y, 79.075 Ma), diamonds (anomaly C32y, 73.004 Ma), triangles (anomaly C30y, 67.610 Ma) and stars (anomaly C25y, 56.391 Ma) (Müller et al., 1999, ages from Gee and Kent, 2007). Thick dotted lines indicate oceanic crust with an estimated age of 93 Ma. Oceanic crust older than 93 Ma should contain black shales deposited during OAE 2. The thin dotted line labeled '120 Ma' indicates a crustal age of 120 Ma (the age of OAE 1). The 93 Ma and 120 Ma crustal ages were derived by linear extrapolation from anomaly 34 assuming the same, constant spreading rate as between anomalies 34 and 33. A plate dip of 42.4 degrees (Syracuse et al. 2010) has been assumed for sections south of the Marathon FZ in order to extrapolate ages west of the trench. Plate dip was considered negligible for age extrapolation beneath the northern sections where the fracture zones are approximately parallel to the trench.

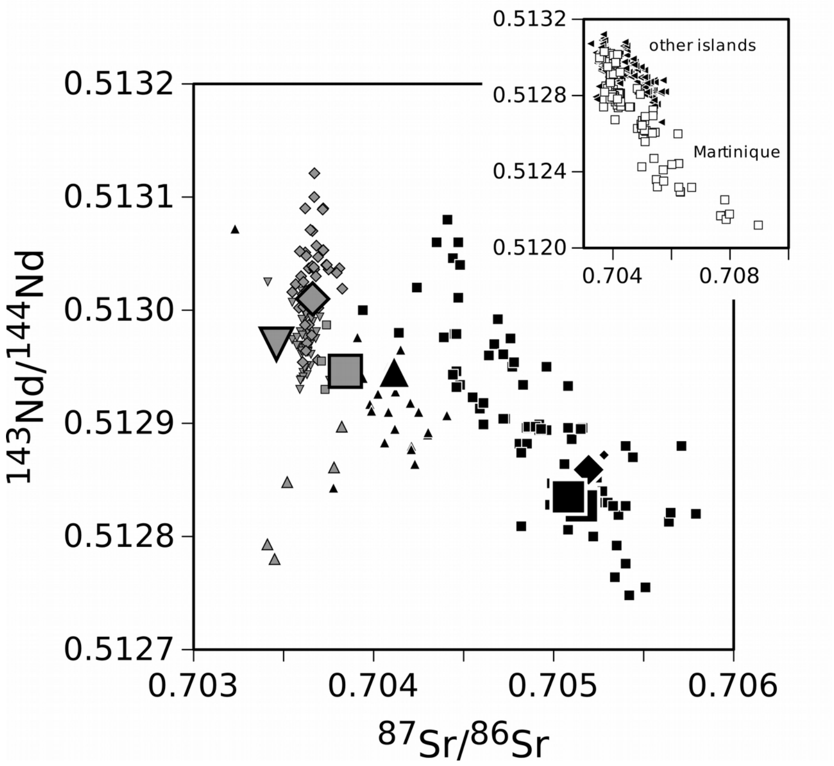

Figure DM2. Radiogenic isotope compositions of northern and southern Lesser Antilles arc lavas. Symbols indicate different islands as defined in Fig. DR1. Large symbols are from this study (Table DR1), small symbols are for previously published data (georoc.mpch-mainz.gwdg.de/). Open symbols in the inset are for samples from Martinique, closed symbols are for samples from other islands.

Table DR1: Mo, Pb, Sr and Nd isotope ratios in Lesser Antilles arc lavas and DSDP Site 144 sediments.

island / site	sample	lithology	Latitude	Longitude	phenocrysts present (a)	sediment unit; thickness (b)	Mo [µg/g]	Ce [µg/g] (c, d)	MgO [wt.%] (c, d)	$\delta^{98/95}$Mo [‰]	2 SE (e)	^{206}Pb/^{204}Pb (d)	2 SE (e)	^{207}Pb/^{204}Pb (d)	2 SE (e)	^{208}Pb/^{204}Pb (d)	2 SE (e)	^{87}Sr/^{86}Sr (c)	^{143}Nd/^{144}Nd (c)
	Lesser Antilles arc lavas																		
Saba	LSS1	basaltic andesite	N 17°38.7'	W 63°12.8'	am, ol, pl		1.10	12.77	7.37	-0.082	0.017	18.913	0.0008	15.633	0.0007	38.621	0.0020	0.70371	-
Saba	*LSS3 (g)*	basalt	*N 17°38.7'*	*W 63°12.8'*	*am, ol, pl*		*1.27*	*8.73*	*11.0*	*-0.087*	*0.021*							*0.70377*	-
Saba	LAS1	basalt	N 17°38.8'	W 63°12.7'	cp, ol, pl		1.01	12.31	8.01	-0.051	0.016	18.935	0.0010	15.639	0.0007	38.656	0.0021	0.70384	0.512946
St. Kitts	LSK2	basaltic andesite	N 17°24.1'	W 62°46.6'	cp, ol, pl		1.04	9.55	4.20	-0.089	0.020	19.016	0.0005	15.660	0.0006	38.759	0.0017	0.70366	0.513010
Montserrat	LSM07	basaltic andesite	N 16°40.6'	W 62°10.5'	cp, ol, pl		1.13	23.12	5.39	-0.051	0.015	18.917	0.0014	15.615	0.0019	38.593	0.0069	0.70346	0.512970
Guadeloupe	GUAD511	basalt	-	-	NA		0.61	8.84	6.61	-0.090	0.020	19.166	0.0004	15.667	0.0005	38.835	0.0014	0.70350	-
Martinique	LSM2	andesite	N 14°43.6'	W 61°05.6'	NA		0.78	20.90	2.98	-0.186	0.016	19.620	0.0006	15.789	0.0008	39.441	0.0030	0.70506	-
St. Vincent	LAV2	basaltic andesite	N 13°19.6'	W 61°10.8'	cp, ol, pl		1.05	14.04	4.15	0.016	0.021	19.314	0.0009	15.720	0.0007	38.925	0.0022	0.70411	0.512946
Grenadines	WIC19	basalt	N 12°17.5'	W 61°35'	NA		1.12	16.09	10.4	0.174	0.018	19.703	0.0009	15.792	0.0011	39.254	0.0032	0.70546	-
Grenada	*LSG5 (g)*	basalt	*N 12°13.7'*	*W 61°36.9'*	*cp, ol, pl*		*0.26*	*57.78*	*8.55*	*0.097*	*0.035*							*0.70424*	-
Grenada	*LSG8 (g)*	basalt	*N 12°08.1'*	*W 61°44.9'*	*cp, ol, pl*		*0.84*	*39.54*	*7.06*	*0.258*	*0.017*							*0.70448*	-
Grenada	*LAG2 (g)*	basalt	*N 12°08.1'*	*W 61°44.9'*	*cp, ol, pl*		*1.15*	*39.05*	*6.86*	*0.336*	*0.017*							*0.70448*	*0.512934*
Grenada	LAG3	basaltic andesite	N 12°14.1'	W 61°39.7'	am, cp, pl		1.43	49.42	5.09	0.228	0.017	19.451	0.0010	15.745	0.0010	39.008	0.0031	0.70515	0.512827
Grenada	LAG4	basalt	N 12°03.7'	W 61°45.3'	ol, pl		0.85	18.11	17.3	0.153	0.016	19.465	0.0006	15.754	0.0006	39.080	0.0023	0.70508	0.512835
	rock standards																		
	JB-2	basaltic andesite					0.89			0.062	0.025 (n = 3) (f)								
	BHVO-2	basalt					4.16			-0.059	0.054 (n =5) (f)	18.646	0.0014	15.491	0.0014	38.207	0.0044		
	AGV-2	trachyandesite										18.907	0.0018	15.615	0.0022	38.568	0.0073		
	DSDP Site 144 sediments																		
DSDP Site 144	144B-2-2W-11.5-13	foram nanno chalk ooze				1; 120 m	0.51	61.2	1.8	-0.355	0.028	19.135	0.0019	15.743	0.0019	39.271	0.0040	0.71097	0.511959
DSDP Site 144	144-3-1W-120–121	slightly zeolitic calcereous mudstone				2; 60 m	0.11	27.1	0.8	-0.555	0.047	20.042	0.0030	15.886	0.0028	39.862	0.0060	0.70869	0.511730
DSDP Site 144	144A-5-1W-119–124	zeolitic calcereous carbonaceous black shale				3; 60 m	41.9	12.8	0.8	0.674	0.030	21.273	0.0041	15.882	0.0029	39.423	0.0070	0.70787	0.511843
DSDP Site 144	144A-6-1W-90–93	zeolitic calcereous carbonaceous black shale				3; 60 m	51.0	13.7	0.7	0.522	0.019	21.691	0.0022	15.925	0.0016	39.422	0.0040	0.70788	0.511832
DSDP Site 144	144-7-1W-125–130	slightly quartzose carbonaceous clay				5; 47 m	0.20	56.3	1.6	0.129	0.048	18.935	0.0015	15.691	0.0016	39.062	0.0040	0.70914	0.512105
DSDP Site 144	average sediment (h)					327 m	7.92	44.1		0.543		19.601		15.784		39.307		0.70851	0.511990

(a) am = amphibole, ol = olivine, pl = plagioclase, cp = clinopyroxene, NA = information not available.
(b) sediment units and thickness as described in Hayes et al. (1972).
(c) Ce and MgO concentrations, Sr and Nd isotope ratios in Lesser Antilles arc lavas are from van Soest (2000).

(d) Ce and MgO concentrations, Sr, Nd and Pb isotope ratios in DSDP Site 144 sediments are from Carpentier et al. (2009).
(e) 2 SE = 2σ standard error (internal measurement error).
(f) n = number of individual analyses measured on separate dissolutions. The error represents the 2 σ standard deviation of the individual measurements.
(g) samples are considered contaminated and are not used in the figure or discussion. See analytical methods for detail.
(h) Bulk DSDP Site 144 sediment composition is the average for the different sediment units weighted by their sediment thickness. For this purpose, DSPD Site 144 Unit 3 (comprising OAE 2 and OAE 3) has been assumed to be made of 50% black shales and 50% sediments similar to those of unit 2, as indicated by the stratigraphic variation in total organic carbon content in this unit (Erbacher et al., 2004). Unit 4 has been assumed to be similar in $\delta^{98/95}Mo$ to unit 2 because both are dominantly made of marl. Average isotope ratios were additionally weighted by the concentration of the respective element in the sediment unit.

Analytical methods

Mo isotope ratios and Mo concentrations were measured using a ^{97}Mo-^{100}Mo double spike following the methods decribed in Freymuth et al. (2015) and Willbold et al. (2016). Mo isotope ratios are reported relative to NIST 3134. The rock standards BHVO-2 and JB-2 were analysed together with the samples. BHVO-2 appears to be isotopically heterogeneous (see Willbold et al., 2016) and we therefore consider the replicate analyses of JB-2 more appropriate as a measure of external reproducibility.

Powders used for Pb isotope analyses were leached in 6 M HCl for 1 hour at 100°C prior to dissolution in HF/HNO_3. Pb was separated from the matrix on AG1-X8 resin using the approach of Strelow and Van der Walt (1981) further described by Galer (1986). Pb isotope ratios were measured using a Neptune MC-ICP-MS at the University of Bristol and corrected for instrumental mass bias by sample-standard bracketing with NBS 981. Ratios assumed for NBS 981 are $^{206}Pb/^{204}Pb$ = 16.9416, $^{207}Pb/^{204}Pb$ = 15.4998, $^{208}Pb/^{204}Pb$ = 36.7249 (Baker et al., 2004).

Pb contamination has previously been described for Lesser Antilles arc lava samples (Thirlwall et al., 1996). We therefore performed additional Pb isotope measurements on sample powders that were not previously leached. Pb isotope ratios measured on leached and unleached powders usually agreed within 1 %. For these samples we assume the Pb isotope ratios measured on leached powders to reflect magmatic values. Pb contamination of samples for which this was not the case was considered too severe for the leaching to fully remove the contaminant. These samples are reported in italics in Table DR1 and were not plotted in Fig. 2. Mo isotope ratios in these samples are similar to those of other samples from the same islands suggesting that Mo was likely unaffected by contamination. We nevertheless took a conservative approach and did not include these samples in plots and the discussion.

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